Publication number : 05-036425

Date of publication of application : 12.02.1993

Int.Cl. H01M 8/02 C25D 3/12 C25D 5/48 C25D 7/00 H01M 8/12

Application number : 03-038935

Applicant : TOKYO ELECTRIC POWER CO INC:THE

Date of filing : 12.02.1991

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ALLOY SEPARATOR FOR SOLID ELECTROLYTIC FUEL CELL AND MANUFACTURE OF THE SAME

[Abstract]

PURPOSE: To economically manufacture a separator having high electric conductivity and durability by forming a separator from a heat resisting alloy material, and providing predetermined plating layers by wet plating on required surfaces of the separator, respectively.

CONSTITUTION: Separators 4, 4' are formed from heat resisting alloy material, and a Ni plating layer and a LaCrO3 plating layer are provided by wet plating on the respective surfaces opposite to a fuel electrode 1 and an air electrode 2 of the separators 4, 4'. These plating layers prevent the formation of oxidized films on the opposite surfaces to the respective

electrodes of the separators, and an alloy separator for solid electrolytic fuel battery economically enhanced in electric conductivity and durability is provided.

[Claims]

[Claim 1] An alloy separator for solid electrolytic fuel cell with high electric conductivity, having a solid electrolyte, a fuel electrode, an air electrode, and a separator, comprising:

a separator consisted of a heat resisting alloy material;

a nickel plating layer formed by a wet plating on the surface having fuel electrode of said separator; and

a $LaCrO_3$ plating layer formed by wet plating on the surface having an air electrode.

[Claim 2] The alloy separator for solid electrolyte fuel cell of Claim 1, wherein the plating layers have a thickness between 3 and 30 μm.

[Claim 3] The method of preparing an alloy separator for solid electrolyte fuel cell with high electric conductivity, having a solid electrolyte, a fuel electrode, an air electrode, and a separator, comprising:

forming a separator by using a heat resisting alloy material;

forming a Nickel plating layer by wet plating on the surface of said separator having a fuel electrode; and

forming a $LaCrO_3$ plating layer by oxidizing a LaCr-based plating layer that has been electro-deposited by wet plating on the surface of said separator having an air electrode.

[Title of the invention]

ALLOY SEPARATOR FOR SOLID ELECTROLYTIC FUEL CELL AND MANUFACTURE OF THE SAME

[Detailed Description]

[Field of the Invention] The present invention relates to a solid electrolytic fuel cell, and more particularly to a method of preparing an alloy separator for solid electrolyte fuel cell with high electric conductivity.

[Description of the Prior Art] Traditionally, a number of electrolyte fuel cell that uses the direct current energy obtain by a chemical reaction process between gas that can easily be oxidized, such as hydrogen, and gas that have oxidizing power, such as oxygen. An example of such is a solid electrolyte fuel cell (solid oxide fuel cell) that uses a solid electrolyte that exhibits ionic electric conduction. The above-mentioned cell has advantages of: not requiring a higher value metal catalyst such as platinum, having a high efficiency of energy transition, and a low quality fuel such as a coal gas can be used. Moreover, since the cell only in a solid form, no problems arise when treating a liquid electrolyte such as a phosphate electrolyte fuel cell or a melting carbonate fuel cell. Another advantage is that the waste heat of the high reaction temperature of the cell ranging from 800 to 1000 °C can be used.

The above-mentioned solid electrolytic fuel cell can be in a plane or a cylinder shape. For example, as the structure of a single plane-shaped solid electrolytic fuel cell shown in Figure 1, a solid electrolyte (e.g. ZrO_2) plate 3 was inserted between a pair of fuel electrodes 1 and an air electrode 2. Then, they were inserted into separators 4 and 4' that have

numerous pairs of long grooves. Such single cells are connected in a series to become a stack, which can provide a practical electric power supply. Moreover, each unit of the fuel cells is separated by the separator 4, which has a function of providing an electrical connection between the fuel cells connected in a series and a function of supplying a pathway for reactant gases (fuel gas and air).

In general, the electrolyte plate 3 is a sintered body, such as a stabilized oxide zirconium; the fuel electrode (anode) 1 is formed of a sintered body of porous nickel; and the air electrode (cathode) 2 is consisted mainly of sintered body of perovskite oxide. Hydrogen is introduced between the fuel electrode 1 and the separator 4 and oxygen and air are introduced between the air electrode 2 and the separator 4', thereby producing electromotive force by the reactions as follows.

Air electrode (reaction on the surface of the electrolyte):

$O_2 + 4e \rightarrow 2O - 2$

Fuel electrode (reaction on the surface of the electrolyte):

$2H_2 + 2O - 2 \rightarrow 2H_2O + 4e$

The separators 4 and 4' is ordinarily formed of ceramic heat resisting alloy and are provided in an orthogonal structure. The opposite plates of the separators 4 and 4' are consisted of multiple long grooves that act as an air or a fuel pathway, to which air or fuel is supplied. As a material for the separators 4 and 4', $LaCrO_3$-based ceramic, such as $LaCrO_3$, Mg-added $LaCrO_3$, Sr-added $LacRO_3$, or heat resisting alloy, such as Fe-Cr based, Fe-

Cr-Ni based, Ni-Cr based, Ni-Cr-Mo based, Fe-Al based, and Fe-Cr-Al based materials are now in trials to be used.

[Object of the Invention]

As described above, the separator needs to achieve an enhanced function of electrical connection between the cells and form a pathway for the passage of fuel and air from the electrode plates. Thus, not only a good electric conductivity is necessary, but also, keeping air separate from fuel gas is necessary. However, because the above-mentioned heat resisting alloy separator is used at a high temperature surrounding 1000 °C, an oxide film (Cr_2O_3, Al_2O_3, SiO_2, etc.) that have the oxides that are based on parent metals (iron or nickel, etc.) and alloy elements as the main structure are both formed. As a result, the electrical conductivity is decreased, and the electrical connection between the electric cells is damaged. Moreover, due to the formation of a thick film at the side of the air electrode, the cell (air electrode/electrolyte/fuel electrode) is destroyed.

Therefore, in order to hinder the formation of the films and to prevent the decrease in the electric conductivity, $LaCrO_3$ based, $LaMnO_3$ based and $LaCoO_3$ based materials were coated using the metal spraying or the slurry coating methods. However, since a fine film could not be easily achieved by using those methods, oxidation of the separator could not be prevented.

[Means to Solve the Problem] In order to prevent the decrease in the

electric conductivity, the inventors of the present invention found that the oxidation of a separator could be prevented by using a wet plating method of any type of metal or metal oxides, and furthermore, that the method also prevents the decrease in electric conductivity. In other words, the present invention provides an alloy separator for solid electrolytic fuel cell having a fuel electrode, an air electrode, and a separator, wherein the separators 4 and 4' are consisted of heat resisting alloy, the fuel electrode 1 of the separator has a nickel plating layer 4a, and the air electrode 2 has a $LaCrO_3$ plating layer 4b by applying a wet plating method. Additionally a method to prepare an alloy separator for solid electrolytic fuel cell having a solid electrolyte, a fuel electrode, an air electrode, and a separator, characterized in making the separator using heat resisting alloy, forming a nickel plating layer on the fuel electrode side of said separator, and forming a $LaCrO_3$ plating layer by oxidizing LaCr-based plating layer, which is electro-deposited using a wet plating method, on the air electrode side of said separator.

According to the present invention, the thickness of the plating layers is preferably 3 to 30 μm and a nickel plating is formed on the fuel electrode using the wet plating method. Moreover, a $LaCrO_3$ plating layer on the air electrode is formed by plating LaCr followed by an oxidation treatment under a real operating condition. If the plating layer is less than 3 μm thick, the prevention of the oxidation is less effective. Furthermore, if the plating layer is more than 30 μm thick, the resistance is enhanced. Therefore, the electrical connection function is prevented enough at a

thickness between 3 to 30 μm.

Moreover, a good result could also be achieved by using cobalt plating instead of the nickel plating. For $LaCrO_3$, it is preferable to use, other than $LaCrO_3$, $La_{0.9}Mg_{0.1}CrO_3$, $La_{0.9}Sr_{0.1}CrO_3$. Furthermore, the same wet plating method can be used.

The sectional structure of the separator can be in the form of one body that has long grooves on both of the fuel electrode side and the air electrode side, an example of which is shown in Figure 2 (A); a three part-type structure having a fuel electrode part, an air electrode part and a heat resisting alloy sandwiched therebetween as shown in Figure 2 (B); and a two part-type structure having a fuel electrode plate and an air electrode plate as shown in Figure 2 (C). In addition, in the figure, 4a is the nickel plating layer and 4b is $LaCrO_3$ plating layer.

[Example] The following is an example of the present invention described in detail.

Ni-Cr-Mo alloy, nickel layer for the fuel electrode, and $LaCrO_3$ layer for the air electrode were used for an alloy separator. For the nickel layer, nickel sulfate ($NiSO_4 \cdot 6H_2O$) bath at 2 to 10 A/dm^2 current density and 20 to 30 μm thickness was used to be electro-deposited. For $LaCrO_3$ layer, [$(NH_4)_2Cr_2O_7$ + $La(NO_3)_3$] bath was used to electro-deposit at an electrical potential (-2.0 V to -1.5 V c sSCE), followed by forming a film having several μm per 1 La/Cr molar ratio and undergoing oxidation between 700

°C to 1000 °C under air.

Figure 3 shows the changes in the generating capacity over a period of time when the alloy separator thusly obtained was used for a solid electrolytic fuel cell. In addition, the same figure also shows the results when an alloy separator without the plating layer.

As shown in the figure, comparing with the alloy separator without the plating layer, the magnitude of the decrease in capacity of the plated alloy separators was much less after a long period of operation. When the alloy separators were observed after the operation, the alloy separator that were plated was seldom changed, while the one without the plating layer showed thick oxide film formed on it. The little degradation of the function of the plated alloy separator was due to a small amount of increase in electric resistance caused by controlled formation of oxide films.

[Effect of the Invention] As explained above, the alloy separator of the present invention prevents the decrease in the electrical connection function at a low cost, and provides a solid electrolytic fuel cell that contains such separator, thereby providing an advantageous electric cell whose capacity does not decrease over a continuous use.

[Brief Description of the Drawing]

[Fig. 1] A perspective exploded illustration of a solid electrolytic fuel cell.

[Fig. 2] A structural sectional view of each type of the separators for a plane-shaped solid electrolytic fuel cell according to the example.

[Fig. 3] A graph showing the changes in the generating capacity over a period of time when the alloy separator with and without plating were used for a solid electrolytic fuel cell.

[Explanation of the References] 1: Fuel Electrode, 2: Air Electrode, 3: Solid Electrolyte Plate, 4, 4': Separator, 4a: Nickel Plating Layer, 4b: $LaCrO_3$ Plating Layer